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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US96/09764 <b>(22) International Filing Date:</b> 7 June 1996 (07.06.96)  <b>(30) Priority Data:</b> 08/473,693 7 June 1995 (07.06.95) US  <b>(71) Applicant:</b> EXXON CHEMICALS PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520-5200 (US).  <b>(72) Inventor:</b> FISHER, Richard, Allen; 2216 Fairwater Park Drive, League City, TX 77573 (US).  <b>(74) Agents:</b> MULLER, William, G. et al.; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US).		<b>(81) Designated States:</b> CA, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> BIMETALLYDIC TRANSITION METAL CATALYST SYSTEMS  <b>(57) Abstract</b>  This invention relates to catalyst systems comprising activated bimetallocyclic transition metal compounds, and the use of these catalyst systems for the polymerization of ethylenically and acetylenically unsaturated monomers. The bimetallocyclic compounds comprise two metal atoms, selected from the group consisting of Group 4 or Group 5 metal atoms, connected through two covalent bridging links so as to form a cyclic compound having delocalized bonding.		

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## BIMETALLYDIC TRANSITION METAL CATALYST SYSTEMS

**Field of the Invention**

5 This invention relates generally to polymerization catalyst systems comprising an activated bimetallocyclic compound, and to a process for polymerizing ethylenically or acetylenically unsaturated monomers. More specifically, this invention relates to the use of certain bimetallocyclic compounds of Groups 4 and 5 of the Periodic Table of Elements (IUPAC new notation) as polymerization catalysts.

10

**Background of the Invention**

There are many known methods and catalysts useful for the homo- or co-polymerization of olefins. For example, in what are generally referred to as a traditional Ziegler-Natta catalyst systems, transition  
15 metal compounds are cocatalyzed by an aluminum alkyl to generate catalysts capable of producing both high and low molecular weight polyolefins. The polymers produced in these systems are characterized by a very broad, sometimes multimodal, molecular weight distributions and, in the case of copolymers, uneven comonomer distribution, largely due to  
20 the presence of multiple sites capable of active polymerization and variances in the chemical stability and reactivity of those sites.

Among the many varieties of Ziegler-Natta catalysts studied, a particular class of catalysts comprising transition metal compounds  
25 possessing two cyclopentadienyl ligands ("metallocenes") cocatalyzed with aluminum alkyls, are known to successfully polymerize  $\alpha$ -olefins. However, the activity of these systems was markedly low until the development of the now well-known metallocene-alumoxane catalyst systems. Furthermore, these alumoxane-activated systems were observed  
30 to produce polymers having narrow Polydispersity Index, or molecular weight distribution ("MWD"), ( $M_w/M_n$ ) in contrast to traditional Ziegler-Natta systems, since the catalyst systems were largely single site catalysts.

35 Since that time, others have developed further these metallocene based catalyst systems. Addition of covalent bridging linkages between the cyclopentadienyl ligands of the metallocene compounds yielded monometallocyclic compounds capable of active polymerization. See, for

example, EP-A-0 129 368 and U.S. patent 5,324,800. Activation of such by ionizing activators yielded saturated bimetallic catalysts see U.S. 5,198,401. Heterocyclic, monocyclopentadienyl transition metal compounds have been shown to be effective olefin polymerization catalysts with both alumoxane and noncoordinating anion precursor activators, see for example U.S. patent 5,055,438 and WO-A-92/00333, which additionally can yield saturated bimetallic catalysts. Though the foregoing are largely restricted to Group 4 transition metal compounds, extension to Group 5 and 6 metal compounds was illustrated in WO-A-94/01471. Cyclic transition metal compounds comprising a Group 4 metal and two amido groups connected by a covalent bridging group containing a Group 14 or 16 element have also demonstrated catalytic activity when activated by alumoxane compounds, see U.S. patent 5,318,935.

Stable bimetallocyclic compounds of the Group 5 metals Niobium and Tantalum have been synthesized and studied as reported in the academic literature. See, "Crystal Structure of Bis- $\mu$ -trimethylsilylmethylidyne)tetrakis-(trimethylsilylmethyl)diniobium(v). A New Type of Carbon Bridging Group", Huq, Mowat and Wilkinson, J. Chem Soc., Chem. Commun., 1477 - 1478( 1971), and "Elimination Stabilized Alkyls. Part III. Trimethylsilylmethyl and Neopentyl Alkyls of Transition Metals", Mowat and Wilkinson, J.C.S. Dalton , 1120 - 1124 (1973). Similar compounds supported on silica have been reported to be active catalysts for the exhaustive hydrogenation of aromatic substrates, see "Surface-supported Group 5 Metal Organometallic Compounds for Catalytic Arene Hydrogenation", Profflet, Rothwell and Rothwell, J. Chem Soc., Chem. Commun., 42 - 44 (1993). Polymerization capability and activity are not reported.

In view of developments in the organometallic field that bulky ancillary ligands can be used to stabilize organometallic compounds of the early transition metals so that they will sustain a cationic charge without decomposing into catalytically inactive species, additional species capable of similar stability were sought. In particular, since each of the above systems in the patent art showed various capabilities with respect to olefin polymerization activities, molecular weight and microstructure capability, including levels of comonomer incorporation in polyethylene

copolymers, new active but stable catalyst systems capable of single site catalysis were sought.

### Summary of the Invention

5        This invention relates to stable single site polymerization catalyst systems comprising an activated bimetallocyclic compound and the use of such catalyst systems to polymerize ethylenically or acetylenically unsaturated monomers. A particular embodiment of the invention includes bimetallocyclic compounds comprising two independently  
10       selected Group 4 or Group 5 metal atoms directly linked through two covalent bridging groups so as to form a cyclic compound having delocalized bonding such that the bimetallocyclic compounds can be activated by cocatalyst compositions into stable, active polymerization catalysts for ethylenically and acetylenically unsaturated monomers. The  
15       invention also comprises a method of polymerization comprising contacting one or more of ethylenically or acetylenically unsaturated monomers with the invention catalyst systems under polymerization conditions to produce polymers with relatively narrow molecular weight distributions and, optionally, high molecular weights.

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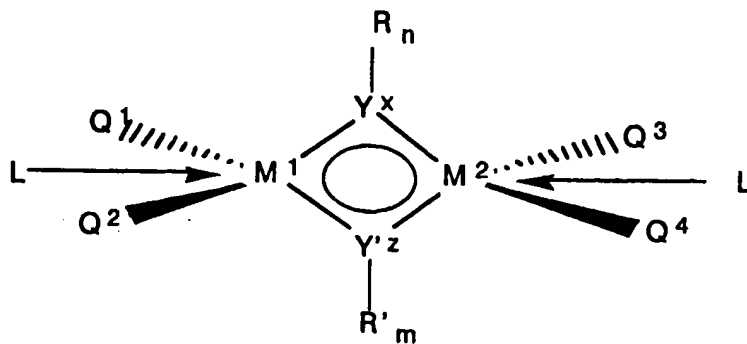
### Detailed Description

      The bimetallocyclic compounds of the invention are characterized by having at least two transition metal atoms in a cyclic structure bound together by delocalized bonding. The delocalized bonding provides a  
25       stabilized structure wherein the metal atoms can carry a cationic charge without becoming so reactive to arbitrary ligand abstraction that catalyst activity is lost. Additionally, it is significant that due to the electron sharing between the two metal atoms and the bridging structure between them, an essentially single site catalyst is formed. Ligand abstraction for  
30       activation thus appears to occur substantially at only one of the two available metal sites (the non-bridging ligand sites), the remaining metal ligand bonds becoming too strongly held for further abstraction. A stable cationic charge thus occurs at one of the metal sites, which serves to facilitate olefinic insertion for polymerization, yet can be charge-balanced  
35       by an effective cocatalyst component. Additionally, the cyclic ligand structure created by the bridging groups appears to make the catalytically active metal site open to monomers of virtually all molecular sizes both allowing for good activity for ethylene polymerization and high

incorporation of higher molecular weight olefinically or acetylenically unsaturated monomers. The individual Group 4 and 5 bimetallocyclic compounds of the invention are structurally similar to the biscyclopentadienyl metallocene compounds of the prior art in possessing a tetrahedral metal center. However, the delocalized bonding in the cyclic structure of this invention serves to reduce the number of total electrons per metal atom so as to increase overall electrophilicity. In particular, the invention's bimetallocyclic compounds are more electron deficient possessing only 10 electrons per metal center compared to 16 electrons in biscyclopentadienyl systems and 14 electrons in the heterocyclic, monocyclopentadienyl transition metal systems. The increased electrophilicity relates directly to the ease by which unsaturated monomers are attracted to the site of polymerization activity, and inserted into a growing polymer chain. This is particularly important for the Group 5 metal compounds of the invention since the Group 5 single site catalysts of earlier developments typically have low polymerization activities.

Exemplary single site polymerization catalyst systems comprise activated bimetallocyclic transition metal compounds of groups 4 or 5 of the Periodic Table of Elements. Preferred bimetallocyclic transition metal compounds may be described as group 4 or 5 metal compounds containing covalent bridging groups linking together the metal atoms in a cyclic structure associated by delocalized bonding.

Most generally, bridged bimetallocyclic transition metal compounds may be represented by formula I:



I



wherein:

$M^1$  and  $M^2$  are independently a group 4 or 5 metal, preferably Ti, Zr, Hf, V, Nb, or Ta, in their highest oxidation state;

5

each  $Y^xR_n$  and  $Y'^zR'_m$  is independently a bridging ligand in which each Y and Y' is independently an element selected from group 14 or 15 of the Periodic Table of Elements; x and z are the common valencies of Y and Y', respectively, such that when Y or Y' is a group 14 element, their valency is defined as 4, and when Y or Y' is a group 15 element, their valency is defined as 3, n and m are the number of substituents necessary to complete the valency of Y and Y' subject to the constraints that when Y or Y' is a group 14 element  $n=x-3$  and  $m=z-3$ , and that when Y or Y' is a group 15 element,  $n=x-2$  and  $m=z-2$ ;

15

each R and R' is, independently, a radical selected from the group consisting of substituted or unsubstituted hydrocarbyl, silyl or germyl radicals, preferably C<sub>1</sub>-C<sub>30</sub> hydrocarbyl, silyl or germyl radicals, substituted with C<sub>1</sub>-C<sub>30</sub> hydrocarbyl hydrocarbyl, silyl or germyl radicals, provided that one or more of the hydrogen atoms on the hydrocarbyl, silyl or germyl radical is replaced by a halogen radical, a silyl radical, an amido radical, a phosphido radical, and alkoxy radical, or any other radical containing a Lewis acidic or basic functionality;

20

25

each Q may be independently any univalent anionic ligand such as a halide, hydride, substituted or unsubstituted hydrocarbyl radicals, substituted or unsubstituted silyl, substituted or unsubstituted germyl, substituted or unsubstituted alkoxy radicals, substituted or unsubstituted aryloxy radicals, substituted or unsubstituted amido radicals, substituted or unsubstituted phosphido radicals, preferably having one to thirty carbon atoms, further provided that two Q together may form a dianionic chelating ligand;

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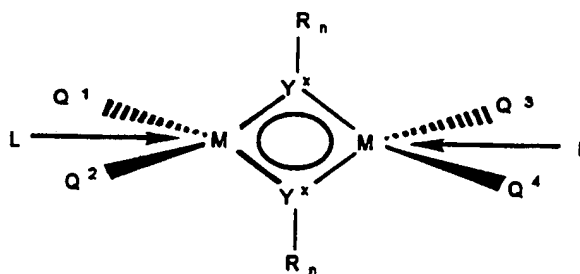
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L is an neutral Lewis base, one or more of which may or may not be present, and which are represented by bases such as diethyl ether,

tetrahydrofuran, dimethylaniline, aniline, trialkyl-  
triarylphosphine and the like.

Typically the hydrocarbyl substituents are most preferred and can  
5 be any of alkyl, aromatic alkylaromatic, arylaromatic, linear, branched or  
cyclic, including both fused and pendant ring systems, preferably having  
from 1 to 30 carbon atoms.

The most preferred embodiment of this invention is represented by  
10 formula II in which  $M_1$  and  $M_2$  are the same transition metal element  
and are bridged



II

15 by identical groups  $Y^xR_n$ . In bimetallo-cyclobutene group 5 catalyst systems,  
these bridging groups are typically alkylidyne group,  $CR_n$  and , where  $R_n$   
is defined as above, for example  $-Si(CH_3)_3$ ,  $-Si(CH_2CH_3)_3$  or  $-Si(t-$   
 $C(CH_3)_3)_3$ . In bimetallo-cyclobutene group 4 catalyst systems, the bridging  
20 groups are typically independently selected from carbene,  $CR_n$  where  $n=2$ ,  
amido or phosphido groups ( $NR_n$ ,  $PR_n$  where  $n=1$ ) where  $R_n$  is  
independently selected from those members of the R and R' groups  
previously defined.

25 The R and R' groups defined above will include such substituents as  
the aliphatic groups methyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl,  
tert-butyl, cyclohexyl, adamantyl, dodecyl, cyclododecyl, and higher alkyls  
or derivatives thereof (e.g., benzyl, diphenylmethyl, or triphenylmethyl),  
the substituted or unsubstituted aromatic substituents such as phenyl,  
30 naphthyl, phenanthryl, and other polycyclic aromatics and their partially  
hydrogenated derivatives (e.g., tetrahydronaphthyl).

The Q groups defined above will include as examples such ligands as the R and R' substituents above and *tert*-butoxy, phenoxy and its alkyl derivatives, dimethylamido, di-*tert*-butylamido, diphenylamido, di-trimethylsilylamido; dimethylphosphido, di-*tert*-butylphosphido, 5 diphenylphosphido, di-trimethylsilyl-phosphido; cyclopentadienyl, indenyl, fluorenyl, and their alkyl and aryl-substituted derivatives; and, bridged cyclopentadienyl Q ligands as previously defined, bridging provided by groups well-known in the metallocene art (e.g., dimethylsilyl, diphenylcarbyl, diethylgermyl, and those consisting of one or more 10 substituted methylene units).

The preferred bimetallocyclic compounds of the invention comprise at least one Group 4 or Group 5 metal having adjacent Q ligands which are capable of either abstraction or replacement by an alkyl group. Upon 15 activation to a monocationic complex, the ligand remaining on the cationic metal center must be capable of olefin insertion. The remaining Q ligands of the other metal center, whether of Group 4 or 5, will be of sufficient bulk or bonding energy that they cannot be abstracted readily by a strong activating cocatalyst component such as methylalumoxane.

20 The activating cocatalysts include, but are not limited to group 13 alkyls, preferably aluminum alkyls; alumoxanes, preferably alkylalumoxanes; and ionizing reagents, preferably Bronsted acid salts, oxidizing metal salts, or covalent neutral compounds containing, or 25 capable of providing, stable, compatible noncoordinating anions. Preferred activating cocatalysts include ionizing activator components which may be ion-exchange compounds comprising a cation, which will irreversibly react with at least one ligand, Q, contained in said transition metal compound and a noncoordinating anion which when functioning as a charge- 30 balancing anion in the catalyst system is compatible, defined as not transferring an anionic substituent or fragment thereof to any cationic species formed as the result of the reaction. One or more of the cocatalyst activators may be used together so long as a Q ligand is abstracted to produce a transition metal cation which is then charge-balanced by the 35 stable, bulky noncoordinating anion. For more information on noncoordinating anion systems, see US Patents 5,198,401 and 5,278,119 see also, EP-A-0 426 637, EP-A-0 495 375 and EP-A- 0 520 732. As described in these documents the cocatalyst precursors may comprise as a

cation portion of the activator component Bronsted acids such as protons or protonated Lewis bases, or may comprise reducible Lewis acids such as ferricinium, tropylium, triphenylcarbenium, or silver cations. Alternatively, the activator may be a neutral Lewis acid capable of abstracting a Q ligand, e.g., tris(pentafluorophenyl)boron, while contributing a counter-balancing noncoordinating anion. Typically these activators require the presence of a Q ligand that is readily abstractable, such as hydride, alkyl or silyl groups.

10 In general, suitable noncoordinating anions for the second component may be any stable and bulky anion or anionic complex typically having the following molecular attributes: 1) the anion is of a bulky size, for example having a molecular diameter about 4 Å or greater; 2) the negative charge should be delocalized over the framework of the anion or be localized within the core of the anion; 3) the anion should be a relatively poor nucleophile; and 4) the anion should not be a powerful reducing or oxidizing agent. Anions meeting these criteria such as boranes, polynuclear boranes, carboranes, metallocarboranes, polyoxoanions, and anionic coordination complexes are fully described in the literature above.

The activator component may also be a Lewis-acid complex which will react with at least one ligand, Q, of the first component, thereby forming an active catalytic species with the ligand from the metal component now bound to the Lewis-acid complex. Alumoxanes, and especially methylalumoxane, the product formed from the reaction of trimethylaluminum with substoichiometric quantities of water, are particularly preferred Lewis-acid second components. By use of an alumoxane, or even an alkylaluminum, as activator either alone or with a noncoordinating anion or precursor above, one or more Q ligand may be halogen, alkoxy or other non-alkyl ligand. Alkylation of the transition metal compound occurs and ionization by ligand abstraction is enabled.

35 Upon combination of the bimetallocyclic transition metal compound and the ionizing cocatalyst compounds above, the second compound, or at least a portion thereof, will react with one of the abstractable nonbridging ligands of the first component, thereby generating an ion pair consisting of the Group 4 or 5 bimetallocyclic transition-metal cation and the

5      aforementioned anion, which anion is compatible with and noncoordinating to the Group 4 or 5 transition-metal cation formed from the bimetallocyclic compound. The anion must generally be capable of stabilizing the Group 4 or 5 transition-metal cations ability to function as a catalyst and must generally be sufficiently labile to permit displacement by an olefin, diolefin, or acetylenically unsaturated monomer during polymerization.

### Catalyst System Preparation and Use

10      The bimetallocyclic compounds of the invention are prepared by conventional procedures as reported in the literature (see Background of the Invention). Thus bis- $\mu$ -(trimethylsilylmethylidyne)tetrakis(trimethylsilylmethyl)ditantalum can be prepared by combining tantalum pentachloride,  $\text{TaCl}_5$ , and a Grignard reagent, e.g.,  
15      trimethylsilylmethylmagnesium chloride,  $(\text{CH}_3)_3\text{SiCH}_2\text{MgCl}$ , in a polar solvent, e.g., diethyl ether, at room temperature. The compound is recovered by filtering, stripping, and recrystallizing from a hydrocarbon solvent. Further derivation is possible, see "Syntheses and Structure of a Di-Tantalum(IV) Hexahydride Compound Containing Ancillary Amido  
20      Ligation", Profflet, *et al*, *Polyhedron Comm.*, v. 11, no. 12, 1559-1561 (1992). Thus any Grignard reagent containing the connecting group - $\text{CH}_2\text{-MgX}$  (where X is halogen), when contacted with the group 5 metal halide may serve as an entry into the bimetallocyclic compounds according to the invention.

25      The Group 4 bimetallocyclic compounds suitable as catalysts when activated as described may be prepared in accordance with procedures well known in the literature. For example, compounds fitting formula II for which  $\text{Q} = \text{NMe}_2$  and  $\text{YR} = \text{N}(\text{tert-butyl})$  have been prepared for  
30      titanium, zirconium, and hafnium (Bradley, D. C., Torrible, E.G., *Can. J. Chem.* 1963, 41, 134-138; Nugent, W. A.; Harlow, R. L. *Inorganic Chem.* 1979, 18, 2030-2032). Other metathetical routes to amido and phosphido complexes of early transition metals are well established, including methods to synthesize bridged complexes (Chisolm, M. H. *et al*,  
35      *Polyhedron* 1988, 7, p. 2215-2220). More recently, sigma-bond metathesis reactions have also been found useful in the synthesis amido complexes of group 4 metals (Uhrhammer, R. *et al*, *J. Amer. Chem. Soc.* 1993, 115, 8493). Group 4 bimetallocyclic compounds of formula II have also been

synthesized by the method of Schmidbaur, see *Z. Naturforschung*, 32b(8), 858-862(1977). Finally, compounds of formula II have been reported by Walsh and Bergman (Walsh, P. J., *et al*, *J. Amer. Chem. Soc.* 1988, 110, 8729). These group 4 bimetallocyclic compounds possess cyclopentadienyl groups corresponding to Q in formula II. These ligands will not be readily abstractable and, therefore, cannot comprise the total complement of Q ligands. As will be appreciated by those skilled in the art, the methodology described by Bergman and Walsh can easily be applied to compounds of formula II. Alternatively, should new methodologies be discovered which allow cyclopentadienyl ligands to readily be abstracted, then compounds such as those described by Walsh and Bergman would serve as viable catalyst precursors as described in this invention.

The catalyst systems employed in this invention are preferably derived from the combining of the bimetallocyclic transition metal compounds of the invention with the activating cocatalyst. Typically convenient preparation of the catalyst system can be accomplished by combining the selected transition metal and activator components, in either order, in an alkane or aromatic hydrocarbon solvent. Alternatively, the bimetallocyclic transition metal compounds of the invention may be activated by first alkylating with an organoaluminium compound, such as an alkylalumoxane or alkylaluminium, and combined with an ionizing activator. In the most preferred processes the solvent utilized for activation would be suitable for use as a diluent for the subsequent polymerization, and when this is the case, the activation may be performed *in situ* in the polymerization reactor. Alternatively, the catalyst system may be prepared separately in either concentrated or dilute form and added to the polymerization reactor containing additional diluent as needed. Solvent systems which are suitable as solvents for the formation of the catalyst system and as diluents for subsequent polymerizations, include but are not limited to, straight and branched chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane, and the like, cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, and the like, and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, xylene and the like. Suitable solvents also include olefins which may act as monomers or comonomers such as ethylene, propylene, 1-butene, 1-hexene and the like,

as well as bicyclic olefins such as norbornene, dicyclopentadiene, and the like.

5 In accordance with this invention, suitable polymerization results are obtained wherein the bimetallocyclic Group 4 or 5 transition metal component is present in the reaction diluent or solvent in a concentration anywhere from  $10^{-5}$  to  $10^{-1}$  mol./l., and the activator component in a concentration such that the ratio of the activator to the bridged bimetallocyclic transition metal component ranges from a molar value of  
10 about 1:1 (typical for discrete noncoordinating anion forming cocatalysts) to about 20,000:1 (highest typical range for alumoxane cocatalysts).

Polymerizations may be conducted by combining the activated transition metal compound with polymerizable monomers. This can be  
15 done in accordance with conventional olefin polymerization conditions well known in the art. In preferred embodiments of the process of this invention, the catalyst system is employed in liquid phase, (slurry, solution, suspension or bulk phase or combination thereof), high pressure liquid or supercritical fluid phase, or gas phase polymerizations of olefin  
20 monomers. These processes may be employed in singular or in series reactors. The liquid processes comprise the steps of contacting an olefin with the catalyst system in a suitable diluent or solvent and allowing said olefin monomer to react with the catalyst system for a time and at a temperature sufficient to produce polyolefin polymer. Bulk  
25 polymerization is typically done by contacting the catalyst with a slurry of liquid monomer, the catalyst typically being supported on a polymeric support or one of a metal or metalloid oxide, such as silica or silica-alumina.

30 The supported catalyst may be prepared in accordance with the knowledge in the art with respect to the use of metallocene catalyst with alumoxane cocatalysts or that addressing the use of metallocenes with noncoordinating anions, for example, the activated catalyst can be supported in accordance with WO 91/0882. In view of the high activity of  
35 the catalysts, use of the methods disclosed in WO 93/11172 or in co-pending U.S. application serial no. 08/285,380, filed 8/3/94, and its equivalent description in WO 96/04319, for preparing ionic catalyst systems chemically bound to the support are preferred. In this last

method a neutral Lewis acid ionizing compound is reacted with hydroxyl group-containing metal oxide supports, preferably complexed with a Lewis base, and then reacted with the transition metal compound which is activated by protonation. Gas phase polymerization will also typically be conducted with supported versions of the invention catalysts. Additionally, the use of scavenging agents, e.g., alkylaluminum or alkylboron compounds, or alkylalumoxanes, is preferred for enhanced activity in accordance with conventional knowledge, see for example, U.S. patent 5,241,025.

10

The catalyst system components may be added to the polymerization vessel separately or after premixing the two components. The catalyst system may be used to polymerize olefins at a wide variety of temperatures. Typically this catalyst system may be used at temperatures from about -100 °C to 300 °C or more, and at pressures of up to 1500 bar, or more. Preferred temperatures include those between about -20 to about 280 °C. However during the formation of the catalyst, temperatures from about 25 to about 100 °C are preferred, with temperatures of about 25 to about 75 °C being most preferred for catalyst formation. A high pressure polymerization utilizing higher temperatures such as that described in U.S. patent 5,408,017 can be effected with the catalysts of this invention as well. The catalyst system components, and the catalyst system once formed, should be protected from exposure to oxygen and water. Therefore the reaction necessary to prepare the catalyst system is preferably performed in an atmosphere which is free of oxygen and moisture, preferably, for example in an atmosphere of dry nitrogen, helium, or argon.

25

Preferred monomers that may be polymerized using the catalyst system of this invention include essentially any monomers having ethylenic or acetylenic unsaturation, particularly the olefinic and acetylenic monomers. Preferred monomers include aliphatic, branched and cyclic olefins and acetylenes. Particularly preferred monomers include C<sub>1</sub> to C<sub>100</sub> α-olefin monomers, preferably linear, branched or cyclic C<sub>1</sub> to C<sub>20</sub> α-olefin monomers, such as ethylene, propylene, butylene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, cyclobutene, cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclononene, cyclodecene, cyclododecene, and alkyl-substituted cyclic

30

35



olefins, substituted and unsubstituted norbornenes, substituted and unsubstituted vinyl norbornenes, styrenes, alkyl-styrenes, para-alkyl-styrenes, a-alkyl-styrenes, 3-methyl-pentene-1, 4-methylpentene-1, 3,5,5-trimethylhexene-1, and the like. Dienes and other polyenes are also  
5 monomers that may be polymerized by the catalyst system described above. Preferred dienes include butadiene, dicyclopentadiene, ethylidene norbornene, methyl norbornene, norbornadiene, 1,5 hexadiene, 1,6 heptadiene, tert-dodecadiene and the like. It will be readily apparent to those of ordinary skill in the art that the monomers listed above can be  
10 homopolymerized, or copolymerized with the other monomers listed.

### Examples

#### Example 1 : Catalyst Synthesis and Polymerization

15 A group 5 compound 1), bis- $\mu$ -(trimethylsilylmethylidyne)tetrakis-(trimethylsilylmethyl) ditantalum, was prepared by mixing tantalum pentachloride,  $\text{TaCl}_5$ , (82.53 mmol.), and trimethylsilylmethylmagnesium chloride,  $(\text{CH}_3)_3\text{SiCH}_2\text{MgCl}$  (453.9 mmol.), in 800 mL. diethyl ether at room temperature. The compound was recovered by stripping, filtering,  
20 extracting into hexane and then cooling at  $-20^\circ\text{C}$  for 12 h. Another Group 5 Compound 2), bis- $\mu$ -(trimethylsilylmethylidynyl)tetrakis(trimethylsilylmethyl)diniobium, was prepared as above substituting  $\text{NbCl}_5$  for  $\text{TaCl}_5$ .

25 a) Methylalumoxane (5.0 ml of a 10 weight percent solution of methylalumoxane in toluene) and compound 1) (1.2 mg dissolved in 1.0 ml toluene) were combined under an inert nitrogen atmosphere and transferred to a one liter autoclave batch reactor which was charged with 400 ml of hexane and 204 psi (1406 kPa) of ethylene. The contents were maintained at  $60^\circ\text{C}$  for 30 minutes, then the polymerization was stopped  
30 by rapidly venting and cooling the reactor. The solid recovered was dried in a vacuum oven at  $80^\circ\text{C}$  for 12 hours. The yield after drying was 10.4 g of polyethylene having  $M_n = 267,000$ ;  $M_w = 650,000$ , MWD = 2.43.

35 b) The procedure of Example 1a was repeated except that compound 2) (1.0 mg dissolved in 1.0 ml toluene) was used in place of compound 1). The yield was 4.0 g of polymer having  $M_n = 340,000$ ;  $M_w = 759,000$ , MWD = 2.23.

**Example 2 : Polymerization**

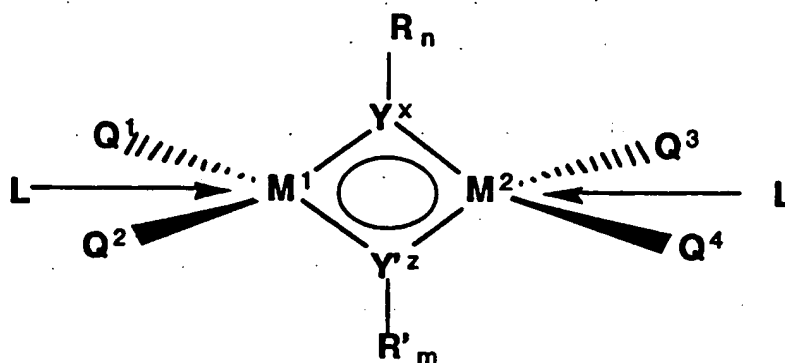
The procedure of example 1 was repeated except that dimethylanilinium perfluorotetraphenyl borate was used in place of methylalumoxane. Compound 1) (0.100g) and the dimethylanilinium perfluorotetraphenyl borate (0.900g) were slurried together in 2.0 ml toluene and gently warmed until the solids were dissolved and a dark oil phase separated out of the mixture. This mixture was transferred to the one liter autoclave batch reactor, which was thereafter charged with 204 psi (1406 kPa) of ethylene. The temperature was maintained at 80 °C. After five minutes an additional 0.100g of compound 1) and 0.900g of dimethylanilinium perfluorotetraphenyl borate, premixed and warmed as before, were added to the reactor. After 30 additional minutes, 10.0g of polymer was obtained,  $M_n = 340,000$ ;  $M_w = 759,000$ ; MWD = 2.24.

As is apparent from the foregoing general description and the specific embodiments, while forms of the invention have been illustrated and described, various modifications can be made without departing from the spirit and scope of the invention. Accordingly, it is not intended that the invention be limited thereby.

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## CLAIMS :

1. A polymerization catalyst composition comprising an activated bimetallocyclic compound, wherein said bimetallocyclic compound comprises two members independently selected from Group 4 or Group 5 metal atoms, those members connected through two covalent bridging links so as to form a cyclic compound having delocalized bonding.
2. The catalyst system of Claim 1 wherein the bimetallocyclic compound is represented by the formula:



wherein:

- $M_1$  and  $M_2$  are independently a group 4 or 5 metal, preferably Ti, Zr, Hf, V, Nb, or Ta, in their highest oxidation state;
- each  $Y^x R_n$  and  $Y'^z R'_m$  is independently a bridging ligand in which each Y and Y' is independently an element selected from group 14 or 15 of the Periodic Table of Elements; x and z are the valencies of Y and Y', respectively, such that when Y or Y' is a group 14 element, their valency is defined as 4, and when Y or Y' is a group 15 element, their valency is defined as 3, n and m are the substituents necessary to complete the valency of Y and Y' subject to the constraints that when Y or Y' is a group 14 element  $n=x-3$  and  $m=z-3$ , and that when Y or Y' is a group 15 element,  $n=x-2$  and  $m=z-2$ ;

- 5 each R and R' is, independently, a radical selected from the group consisting of substituted or unsubstituted hydrocarbyl radicals, preferably C<sub>1</sub>-C<sub>30</sub> hydrocarbyl radicals, substituted with any additional C<sub>1</sub>-C<sub>30</sub> hydrocarbyl radicals, provided that one or more of the hydrogen atoms on the hydrocarbyl radical is replaced by a halogen radical, a silyl radical, an amido radical, a phosphido radical, and alkoxy radical, or any other radical containing a Lewis acidic or basic functionality;
- 10 each Q may be independently any univalent anionic ligand such as a halide, hydride, substituted or unsubstituted hydrocarbyl radicals, substituted or unsubstituted silyl, substituted or unsubstituted alkox radicals, substituted or unsubstituted aryloxy radicals, substituted or unsubstituted amido radicals, substituted or
- 15 unsubstituted phosphido radicals, preferably having one to thirty carbon atoms, further provided that two Q together may form a dianionic chelating ligand; and
- 20 L is an neutral Lewis base, one or more of which may or may not be present.
3. The catalyst system of Claim 2 wherein M<sub>1</sub> and M<sub>2</sub> are independently Ti, Zr, Hf, V, Nb or Ta.
- 25 4. The catalyst system of Claim 2 wherein each R and R' is, independently, a C<sub>1</sub>-C<sub>20</sub> hydrocarbyl radical or a substituted C<sub>1</sub>-C<sub>20</sub> hydrocarbyl radical.
- 30 5. The catalyst system of claim 2 wherein each Q is, independently, a halide, a hydride, a substituted or unsubstituted hydrocarbyl radical, a substituted or unsubstituted alkoxy, a substituted or unsubstituted aryloxy, a substituted or unsubstituted amido, or a substituted or unsubstituted phosphido radical.
- 35

6. The catalyst system of Claim 2 wherein each L is independently selected from diethyl ether, tetrahydrofuran, dimethylaniline, aniline, and trialkyl- triarylphosphine.
- 5 7. The catalyst system of Claim 2 wherein  $M_1$  and  $M_2$  are the same transition metal element and are bridged by identical groups YR.
8. The catalyst system of Claim 7 wherein  $M_1$  and  $M_2$  are selected from group 5 and both YR groups are alkylidyne.
- 10 9. The catalyst system of Claim 7 wherein  $M_1$  and  $M_2$  are selected from group 4 and both YR groups are carbenyl, amido, or phosphido groups.
- 15 10. The catalyst system of Claim 1 wherein the activating cocatalyst is an alumoxane.
11. The catalyst system of Claim 1 wherein the activating cocatalyst is an ionizing activator capable of providing a compatible noncoordinating anion.
- 20 12. The catalyst system of Claim 10 wherein the activating cocatalyst is methylalumoxane.
- 25 13. The catalyst system of Claim 11 wherein the activating cocatalyst is dimethylanilinium perfluorotetraphenylboron or tris(perfluorophenyl)boron.
- 30 14. A process for polymerizing ethylenically or acetylenically unsaturated monomers comprising contacting said monomers under polymerization conditions with a catalyst system according to Claim 1.
- 35 15. The process of Claim 14 wherein the bimetallocyclic compound is represented by the formula according to Claim 2.

16. The process of Claim 15 wherein the activating cocatalyst is methylalumoxane.
- 5 17. The process of Claim 15 wherein the activating cocatalyst is an ionizing activator capable of providing a compatible noncoordinating anion.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/09764

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C08F10/00 C08F4/62

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP,A,0 664 394 (MITSUI) 26 July 1995 see page 26; example 1 see page 22; example I see page 21; example I see page 17; example II see page 12; example II see page 9; example IA ---	1
A	EP,A,0 420 436 (EXXON) 3 April 1991 see claim 6 ---	1
A	EP,A,0 423 872 (AKZO) 24 April 1991 see claims 1,7 see figure 1C -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Inter national Application No

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